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# The Hydrogen Bond, the Halogen Bond and Rotational Spectroscopy: A Personal Retrospective

Anthony Legon<sup>\*</sup>

**Abstract** | This article is a personal, chronological account of experimental work carried out on the hydrogen bond, the halogen bond and other non-covalent interactions by my research group using (mainly) rotational spectroscopy since 1974. It is not intended to be comprehensive, and therefore does not include contributions made by many groups in the last 40 years or so.

## 1 University College London 1970–1984

My first attempt to observe the rotational spectra of hydrogen-bonded complexes was made in 1965/1966 while I was a Ph.D. student at University College London, working with Professor Jim Millen. Jim, a student of C. K. Ingold, had established in 1946, by Raman spectroscopy, the existence of the nitronium ion  $\text{NO}_2^+$  as a linear molecule in nitrating mixtures of nitric/sulphuric acids. In the 1950s, Jim investigated hydrogen-bonded complexes such as  $(\text{CH}_3)_2\text{O} \cdots \text{HF}/\text{HCl}$  in the gas phase by infrared spectroscopy. He established the important result that the breadth of the  $\nu=1 \leftarrow 0$  band associated with the HX stretching mode was not, as had been assumed at the time, either predissociation broadening caused by a very short lifetime of the hydrogen-bonded species or attributable to Fermi resonance. He showed that, in fact, it was caused by sum and difference bands involving a low-frequency intermolecular mode and the HX stretching mode.<sup>1</sup> In 1965, he decided to bring the power of microwave spectroscopy (a technique he learned about while a Commonwealth Fund Fellow working in E. Bright Wilson's group at Harvard in 1951) to bear on hydrogen-bonded complexes. This task was assigned to me.

The microwave spectrometer in the Chemistry Department at UCL in 1965 was of the Stark-modulation type. A klystron was the source of (monochromatic) radiation. Its oscillation frequency was changed by manually adjusting the size of its resonant cavity. By applying a sawtooth voltage to the reflector electrode of the klystron, the cavity mode could be swept over a small

frequency range. The radiation was detected, after passage through an absorption cell, by a crystal diode whose output was displayed on an oscilloscope swept synchronously by the sawtooth voltage. The absorption cell was a waveguide of small cross-sectional area, of length about 3 m and carrying a centrally placed Stark electrode that ran the length of the cell. The approach was to place a gas mixture of a Lewis base B and a hydrogen bond donor HX in the cell and search for the rotational spectrum of the complex  $\text{B} \cdots \text{HX}$  in the equilibrium gas mixture:



Many problems were encountered. It was difficult to prepare a gas mixture, get it into the cell and then avoid differential absorption on the walls. The standard molar enthalpy of reaction (1) is typically  $\Delta H_m^\ominus \approx -10$  to  $-30 \text{ kJ mol}^{-1}$  for hydrogen-bonded complexes, which implies a small equilibrium constant  $K_p^\ominus$  at room temperature, and hence a small partial pressure of complex. One way of increasing the partial pressure is to increase the total pressure of the gas mixture, but microwave spectroscopy is conducted at low pressure to avoid pressure broadening of transitions. Moreover, when the Stark modulation technique is used, too high a gas pressure leads to a discharge between the Stark electrode and the cell wall. This tends to destroy the cell contents. Another way is to increase the equilibrium constant by lowering the temperature, as indicated by the relationship  $d \ln K_p^\ominus / dT = \Delta H_m^\ominus / RT^2$ . However, at temperatures for which  $K_p^\ominus$  is large enough to give a detectable partial pressure of

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complex, the gas mixture tends to condense. A uniform cell temperature is important because the vapour pressure is controlled by the coldest spot in the cell.

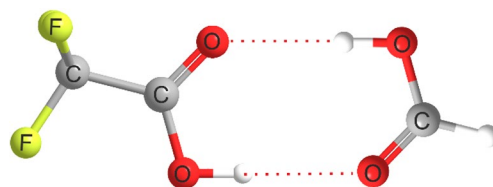
The foregoing paragraph indicates that, at that time, to observe the microwave spectrum of a complex in an equilibrium gas mixture was a significant challenge. It involved tuning the klystron manually, changing the reflector voltage to maintain a cavity mode, ensuring a uniform temperature throughout the waveguide cell to avoid condensation of the gas mixture, controlling the gas pressure and the Stark voltage to avoid a discharge, all the while looking for weak transitions on an oscilloscope. We failed to observe the spectrum of any of the complexes that were attempted, but this led to a chapter in my Ph.D. thesis<sup>2</sup> that later proved useful. The chapter analyses the factors that would make rotational transitions of a complex  $B \cdots HX$  in a gas mixture most readily observable. The conclusions were that (a) the components B and HX should not have rotational spectra in the spectral region examined (no complex background spectra among which to seek weak transitions of the complex), (b) the component molecules should be simple, leading to a complex that is a linear or symmetric-top molecule, and each component should have a large electric dipole moment (this means a favourable partition function, a very large electric dipole moment and transitions of high intensity), and (c) the components should be volatile to avoid condensation. The system  $CH_3CN \cdots HF$  fulfilled these criteria and was viewed as the most promising candidate (see later).

The first hydrogen-bonded complex whose rotational spectrum was observed in the microwave region was the cyclic bimolecule containing two hydrogen bonds<sup>3</sup> (see Fig. 1) and formed between formic acid and trifluoroacetic acid. The value of  $\Delta H_m^\ominus = -66 \text{ kJ mol}^{-1}$  determined later<sup>4</sup> for the association reaction is large as a consequence of the two hydrogen bonds and the spectrum is, therefore, very strong. Unfortunately, only a series of very broad lines containing much unresolved substructure was observed and these were fitted by the pseudo-symmetric-top expression  $\nu = (B + C)(J + 1)$ .

The first high-resolution rotational spectrum of a hydrogen-bonded complex was reported by Klemperer, Dyke and Howard in 1972.<sup>5</sup> They used supersonic expansion of hydrogen fluoride through a simple nozzle to produce a molecular beam at an effective temperature of  $\sim 1 \text{ K}$  in a molecular-beam, electric-resonance spectrometer. In this way, they were able to detect the

radiofrequency and microwave spectra of HF dimer but avoided the problems of low concentrations in equilibrium gas mixtures mentioned earlier. With an outstanding analysis, they were able to interpret the observed splitting of rotational energy levels deduced from the experimental  $(HF)_2$  spectrum in terms of a unique hydrogen tunnelling motion involving the breaking and reforming of the hydrogen bond.

In 1970, I was appointed to a Lectureship in Chemistry at University College London. At about the same time, a Hewlett-Packard 6480A, Stark-modulated, microwave spectrometer was purchased by the Chemistry Department. This superb instrument had backward-wave oscillators as the monochromatic radiation source. Such oscillators could be swept continuously (without operator intervention) over their entire frequency range. Jim Millen and I decided that this technological advance meant that searching for the rotational spectra of hydrogen-bonded complexes did not suffer with the problems mentioned earlier, namely that the operator did not need to fiddle with klystron modes and manual tuning and could, therefore, concentrate on sample handling. The waveguide cells associated with the HP8460A instrument had a very uniform spacing between the Stark electrode and the cell wall, thereby allowing a stable and uniform electric field to be applied to a sample. This yielded beautiful Stark patterns for low  $J$  transitions. Moreover, the cell was more compact than hitherto employed and allowed us to develop a cooling system that gave fine control of temperature, extending from room temperature down to about 200 K. The absorption cell was enclosed by an insulated jacket into which liquid nitrogen could be pumped from a pressurised container at a rate controlled by a sensing platinum resistance thermometer. The liquid nitrogen was delivered at eight points onto a baffle plate above the absorption cell. The combination of a more sophisticated spectrometer and controllable cooling allowed us to search for



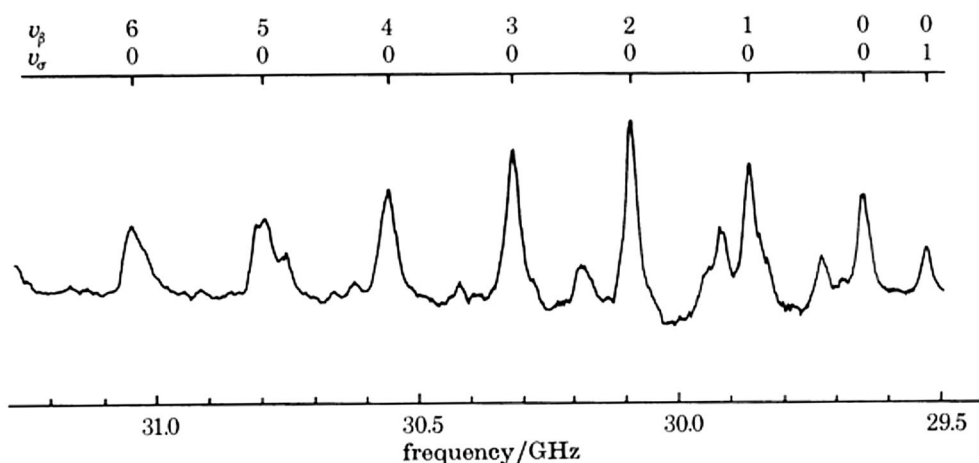
**Figure 1:** A bimolecule formed between trifluoroacetic acid and formic acid. This appears to be the first complex involving intermolecular hydrogen bonds to have been identified by rotational spectroscopy (see Refs. [3,4]).

hydrogen-bonded complexes at temperatures that yielded a sufficiently large equilibrium constant while avoiding condensation of the gas mixture via the complex.

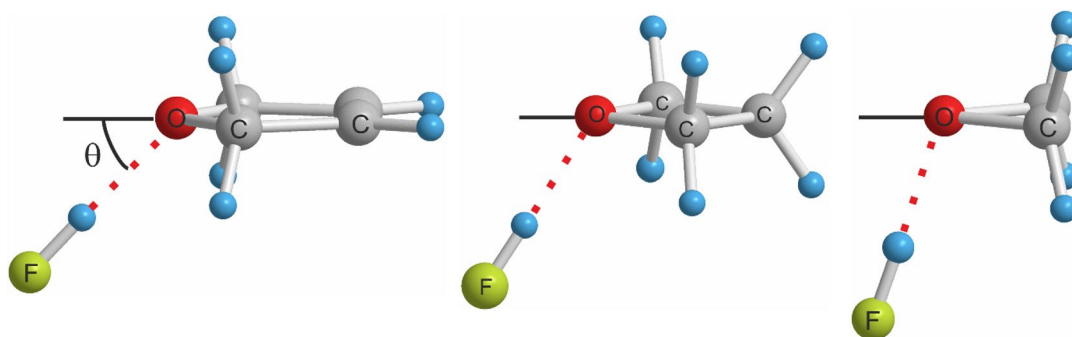
The first search attempted was for the complex formed between methyl cyanide and hydrogen fluoride, the system that best satisfied all the criteria set out in the final chapter of my Ph.D. thesis. The spectrum of  $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{HF}$  was detected in 1974<sup>6</sup> by two remarkably determined and able research students, the late John Bevan (1946–2016) and Stephen Rogers. It consisted of one set of equally spaced, very broad lines. This result was initially viewed as disappointing. Was the breadth caused by a very short collisional lifetime of the complex in the cell and hence irreducible? Fortunately, someone turned up the Stark voltage too far and caused a discharge through the gas mixture, thereby reducing its pressure. Each broad line became resolved into a beautiful pattern consisting of a ground-state transition accompanied by an extended progression of vibrational satellites, as shown in Fig. 2.<sup>7</sup> Each feature corresponds to the  $J=8\leftarrow 7$  transition of the symmetric-top molecule  $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{HF}$ , either in the ground state or in a vibrationally excited state associated with one of the two low-frequency, intermolecular modes  $\nu_\sigma$  (stretching) and  $\nu_\beta$  (bending). Measurement of relative intensities led to vibrational separations in these modes. By observing the spectra of a wide range of isotopically substituted species of the complex, a detailed geometry was determined.<sup>7</sup>

There followed a period of several years in which a series of such hydrogen-bonded complexes  $\text{B}\cdots\text{HF}$  was investigated, all complexes involving HF as the proton donor, mainly because only in those cases was the binding strong enough to yield rotational spectra of observable intensity in equilibrium gas mixtures. The series included  $\text{H}_2\text{O}\cdots\text{HF}$ ,<sup>8, 9</sup>  $\text{HCN}\cdots\text{HF}$ ,<sup>10</sup>  $(\text{CH}_2)_2\text{O}\cdots\text{HF}$ ,<sup>11</sup>  $(\text{CH}_2)_3\text{O}\cdots\text{HF}$ <sup>12</sup> and  $(\text{CH})_2(\text{CH}_2)_2\text{O}\cdots\text{HF}$ ,<sup>13</sup> the last three of which involve the cyclic ethers oxirane, oxetane and 2,5-dihydrofuran, respectively. The cyclic ethers were chosen deliberately to test some rules for predicting angular geometries that were evolving at that time. The rules required the electrophilic atom  $\text{H}^{\delta+}$  of the HF molecule to seek the directions of non-bonding electron pairs. The accepted view was that, as the C–O–C ring angle of the cyclic ether decreased from nearly tetrahedral in 2,5-dihydrofuran, through  $\sim 90^\circ$  in oxetane to  $\sim 60^\circ$  in oxirane, the angle between the  $n$ -pairs on O should increase. We found that the angle made by the HF axis with the bisector of the C–O–C internal ring angle did indeed increase in this way, as shown in Fig. 3 This result was an important factor in formulating the rules, which Millen and I published in 1982.<sup>14</sup>

In the cases  $\text{B}=\text{H}_2\text{O}$ <sup>15</sup> and  $\text{HCN}$ <sup>16</sup>, the simplicity of the components allowed a wide range of properties of the complexes to be determined from measurements of the rotational spectra, of several isotopic species. These included vibrational separations in the intermolecular bending and stretching modes from measurement of intensities



**Figure 2:** Vibrational satellites in the  $J=8\leftarrow 7$  transition in the rotational spectrum of the hydrogen-bonded molecule  $\text{H}_3\text{C}-\text{C}\equiv\text{N}\cdots\text{HF}$ . The satellites correspond to the indicated vibrationally excited states of either the intermolecular bending mode  $\nu_\beta$  or the intermolecular stretching mode  $\nu_\sigma$  (Reproduced from Ref. [7], with permission).



**Figure 3:** Angular geometries determined by rotational spectroscopy for complexes of 2,5-dihydrofuran, oxetane and oxirane with HF. The drawings are to scale and the angles  $\theta$  are  $48.5^\circ$ ,  $57.9^\circ$  and  $72.6^\circ$ , respectively, which implies angles of  $97.0^\circ$ ,  $115.8^\circ$  and  $145.2^\circ$ , respectively, between the two equivalent non-bonding ( $n$ ) electron pairs carried by O, assuming that HF lies along a  $n$ -pair direction in each complex. The angle  $2\theta$  clearly increases as the C–O–C ring angle decreases from  $\sim 108^\circ$ , through  $\sim 90^\circ$  to  $\sim 60^\circ$  along the series. The work on oxirane and oxetane was carried out by Andreas Georgiou, another excellent early group member.

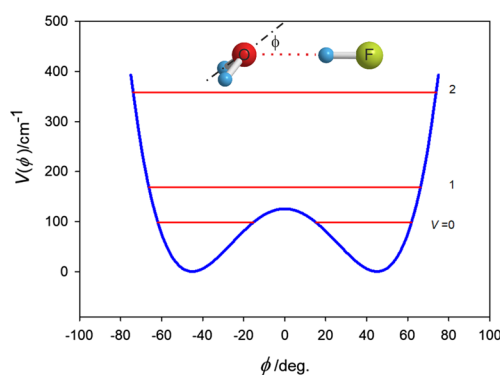
of vibrational satellites relative to that of the corresponding ground-state transition, dissociation energies  $D_0$  and  $D_e$  from absolute intensities of ground-state transitions of the various monomers and the complex in the equilibrium gas mixture, electric dipole moments and their enhancement on complex formation (from Stark effect measurements), potential constants and geometries. A detailed review of how these properties were determined for  $\text{HCN}\cdots\text{HF}$  is available.<sup>16</sup>

For  $\text{H}_2\text{O}\cdots\text{HF}$ <sup>15</sup>, the variation of vibrational separations and of the rotational constants with vibrational quantum number of the low-frequency bending mode allowed the potential energy function shown in Fig. 4 for the out-of-plane bending motion (described by the angle  $\phi$ ) to be established, with the revealing result that, although the complex is effectively planar in the zero-point state, it is definitely pyramidal in the equilibrium conformation. This conclusion was an important element in connection with the above-mentioned rules for predicting angular geometries and was deduced by the careful experimental and computational analysis carried out by Zybsyk Kisiel.

The period from 1974 to 1980 was a scientifically exciting and happy time. Jim Millen and I took great pleasure in planning our research, in discussing its progress and in writing the hydrogen-bonding series of papers; moreover, we were blessed with very able research students. I had the highest regard for Jim as a man, a scientist, a colleague and a friend. He was truly a remarkable scholar and a gentleman.

On one snowy day in January 1979, we had a visit from Willis (Bill) Flygare, who was spending

some sabbatical leave in the UK. Bill was already famous as a chemical physicist; he was elected a Member of the United States Academy of Sciences at the early age of 37 in 1974. He showed interest in our experiments with hydrogen-bonded complexes and asked whether I had any sabbatical leave due and whether I would like to spend it with him at the University of Illinois in Champaign-Urbana. I answered yes to both questions and we agreed that my family and I would arrive in Urbana in August 1979. Our arrival was in fact postponed because of the birth of our second child and we eventually arrived in Urbana on 3 January 1980, in the middle of the mid-west



**Figure 4:** The variation of the potential energy and associated vibrational energy levels with the angle  $\phi$  (defined as indicated) of the complex  $\text{H}_2\text{O}\cdots\text{HF}$ , as determined from rotational transitions in the ground state and in several vibrationally excited states associated with the low-frequency intermolecular bending mode  $\nu_\beta$  (see Ref. [15]).

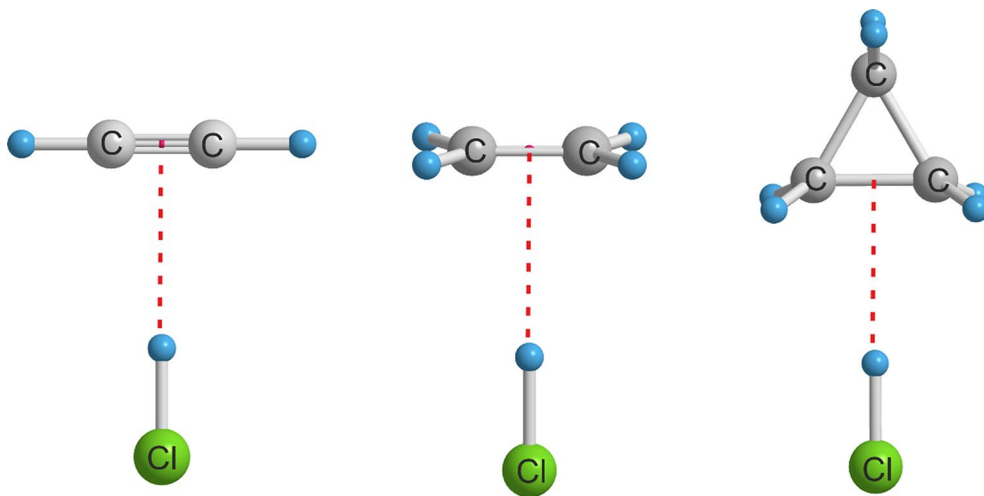
winter, with two children of ages 2.5 years and 7 weeks. It turned out that the reason for Bill's invitation (that his group had been trying to observe the rotational spectra of hydrogen-bonded complexes, but without success) became irrelevant in the summer of 1979 when Bill's graduate student Terry Balle transformed the group's earlier development of Fourier-transform (FT) microwave spectroscopy by replacing the waveguide cell with a Fabry–Perot cavity. Moreover, Balle had managed to incorporate a pulsed nozzle (a solenoid valve) as a means of introducing very low-temperature molecules/complexes into the cavity. This novel combination allowed, for example, the rotational spectra of rare-gas complexes to be detected with a remarkable combination of high resolution and high sensitivity, as illustrated in their July 1979 paper on  $\text{Kr}\cdots\text{HCl}$ <sup>17</sup>, the first publication with the new instrument.

Thus, when I arrived in Urbana, it was a time of great opportunity. Bill asked me what I would like to do. His group were working exclusively on rare-gas $\cdots\text{HX}$  ( $\text{X} = \text{F}, \text{Cl}$  or  $\text{Br}$ ) complexes, while my interests were in more chemical interactions. We began with the complexes  $\text{OC}\cdots\text{HX}$  ( $\text{X} = \text{F}, \text{Cl}$  and  $\text{Br}$ ), mainly because the properties of  $\text{CO}$  gas are not unlike those of the inert gases. Interpretation of observed spectra showed these to be linear molecules, with  $\text{HX}$  forming a hydrogen bond to the carbon atom.<sup>18–20</sup> I then decided to try to answer the question: Is it possible to detect complexes formed by hydrogen halides with  $\pi$ -electron pairs instead of non-bonding electron pairs? We discovered complexes of ethyne and ethene with  $\text{HCl}$ .<sup>21, 22</sup> The shapes of these complexes were proven unambiguously to be those

predicted if the  $\text{HCl}$  molecule forms a hydrogen bond to a  $\pi$ -electron pair, with the  $\text{HX}$  molecules lying along the  $\text{C}_2$  axis, as shown in Fig. 5.

Later, we aimed to discriminate between the pseudo- $\pi$  bond model of cyclopropane in which  $\text{sp}^3$  hybrid orbitals of two adjacent  $\text{C}$  atoms overlapped to produce bent or pseudo- $\pi$   $\text{C}-\text{C}$  bonds (as postulated by Coulson and Moffitt) and the Walsh model which postulated overlap of three  $\text{sp}^3$  hybrid orbitals (one from each  $\text{C}$  atom) in the centre of the ring. According to the former model, the electrophilic region ( $\text{H}^{\delta+}$ ) of  $\text{HX}$  should seek the nucleophilic region at the centre of the  $\text{C}-\text{C}$  bond to give an asymmetric-rotor complex of  $\text{C}_{2v}$  symmetry, but if the Walsh model were to hold, the centre of the ring might provide the most nucleophilic region and consequently the complex might be a symmetric-top molecule, with the  $\text{HX}$  molecule lying along the  $\text{C}_3$  axis of cyclopropane. The geometry determined from the rotational spectra<sup>23</sup> showed that the lowest energy form of the cyclopropane $\cdots\text{HX}$  complexes is of the Coulson–Moffitt, pseudo- $\pi$  type (see Fig. 5).

The year 1980 was also one of sadness. Bill was diagnosed with amyotrophic lateral sclerosis in 1978 and he knew it was a terminal illness. When I arrived at the University of Illinois in January 1980, the effects of the disease were barely noticeable. By the time I left at the end of December of that year, he had almost lost his power of speech and could be understood only with difficulty; he had lost control of his hands and could barely walk. He bore all this with fortitude and grace. He struggled into the laboratory every day until just before he died in May 1981. His enthusiasm for his research never dimmed. I admired



**Figure 5:** Angular geometries of  $\pi$ - and pseudo- $\pi$  complexes formed by ethyne, ethene and cyclopropane with  $\text{HCl}$  (drawn to scale). See Refs. [21–23] for details.



him immensely, both as an outstanding scientist and as a person who showed me and my family much kindness. We got on very well together and became friends, surprisingly because he was confident, uncompromising, hardworking and ambitious American, while I was a quiet, diffident Englishman. I was fortunate to know him and to be given the opportunity to collaborate with him.

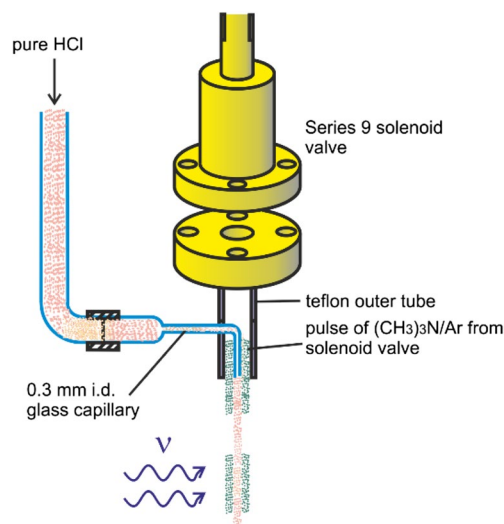
I returned to University College London in January 1980 determined to build a duplicate of the Balle–Flygare spectrometer. It came on-stream in early 1982, thanks mainly to the expertise of Charles Willoughby and the skills of the Chemistry Department's Mechanical Workshop. The first complexes examined with the new spectrometer were  $\text{H}_3\text{P}\cdots\text{HX}$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ )<sup>24</sup> and  $\text{H}_2\text{O}\cdots\text{HX}$  ( $\text{X}=\text{Cl}$  and  $\text{CN}$ )<sup>25, 26</sup>. In 1982, Jim Millen and I gave a paper<sup>14</sup> at Faraday Discussion 73 held in Oxford entitled 'Van der Waals Molecules'. This paper reviewed our earlier work on the rotational spectroscopy of hydrogen-bonded complexes in equilibrium gas mixtures and the results obtained working with the pulsed-nozzle, F–T microwave spectrometer whilst I was at the University of Illinois, and ended with the proposal of a set of rules for predicting the angular geometries of such complexes.

## 2 University of Exeter 1984–2005

In 1984, I moved to the Chair of Physical Chemistry at the University of Exeter. Two talented research students (Elizabeth Goodwin and Annette Fillery-Travis) moved with me and ensured that the momentum in the area of hydrogen-bonding was preserved. My group continued to work on hydrogen-bonded complexes for the next several years, sometimes testing the rules for predicting angular geometries and other times looking for further generalisations that could be made for such non-covalent interactions. There was, in the years between 1982 and 1990, a rapid increase in the number of pulsed-nozzle, F–T microwave spectrometers around the world and a rapid increase in the number of hydrogen-bonded complexes investigated. Bill Klemperer and his group of talented graduate students at Harvard continued to make seminal contributions to the area using their technique of molecular-beam, electric-resonance spectroscopy. Bill preferred the molecular orbital approach for explaining the geometry of the complexes and stoutly defended his view<sup>27</sup> when David Buckingham and Patrick Fowler put forward their electrostatic model for predicting angular geometries. The model is based on a distributed multipole

analysis of the charge distributions of the B and HX molecules involved.<sup>28</sup>

Our work in Exeter on hydrogen-bonded complexes between 1984 and 1993 culminated in a series of detailed studies of the ammonium and methylammonium halides in the gas phase, whose aim was to discover whether the extent of proton transfer from HX to the amine subunit in gas-phase complexes such as  $\text{H}_3\text{N}\cdots\text{HCl}$  could be measured.<sup>29</sup> Unfortunately, pre-mixing of the amine and HX is not possible because of the rapid and unavoidable precipitation of the solid adduct (a familiar phenomenon in chemistry laboratories when bottles of concentrated hydrochloric acid and aqueous ammonia solutions are present and their leaked vapours meet). To overcome this difficulty, we initially observed complexes by vaporising solid ammonium or trimethylammonium halide in a heated nozzle and entraining the vapour in pulses of argon. Later, a so-called fast-mixing nozzle was used, a version of which is shown schematically in Fig. 6. It consists of two concentric tubes attached to the outlet of a solenoid valve. In this device, a pulse of, say, trimethylamine in argon from the solenoid valve enters the outer tube, while an HX flows continuously through the inner of the concentric tubes. The two gas flows meet only as they expand into the evacuated Fabry–Perot cavity. At the junction of the two concentric flows, complexes  $(\text{CH}_3)_3\text{N}\cdots\text{HX}$  are formed, but without significant aggregation to cause precipitation



**Figure 6:** The mixing nozzle used to observe the rotational spectra of complexes such as  $(\text{CH}_3)_3\text{N}\cdots\text{HX}$  (see Ref. [29]) and thereby avoid precipitation of the solid that attends normal pre-mixing of the components.

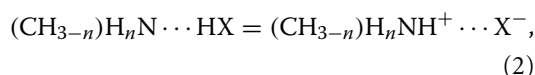
of the solid trimethylammonium halide. The rotational spectra of complexes of the type  $(\text{CH}_3)_{3-n}\text{H}_n\text{N}\cdots\text{HX}$  ( $n = 0$  or  $3$ ) could then be recorded as usual.

A detailed account of this work is given in Ref. [29]. The following is a summary of the main conclusions about the extent of proton transfer deduced.

A key indicator of the extent of proton transfer in a gas-phase complex  $(\text{CH}_3)_{3-n}\text{H}_n\cdots\text{HX}$  ( $n=0$  or  $3$ ) is the magnitude of the halogen nuclear quadrupole coupling constant  $\chi_{aa}(\text{X})$ . For example, it is well known that this coupling constant has the value of  $-5.64$  MHz in NaCl but for HCl the value is  $-67.61$  MHz, both in the gas phase. The Townes–Dailey model for interpreting nuclear quadrupole coupling constants established that NaCl should be described as about 100%  $\text{Na}^+ \text{Cl}^-$  in valence bond terms, while HCl requires the description 62% covalent H–Cl and 38% ionic  $\text{H}^+ \text{Cl}^-$ . Thus, halogen nuclear quadrupole coupling constant might provide a simple, if approximate, measure of the contribution of the ionic valence-bond structure in the ammonium and methyl ammonium halides. Even in a hydrogen-bonded complex such as  $\text{HCN}\cdots\text{HCl}$ , however, there will be a decrease in magnitude of the Cl nuclear quadrupole coupling constant relative to that of free HCl because of the electric field gradient at the Cl nucleus arising from the presence of the HCN charge distribution nearby and this effect must be taken into account.

If  $\text{HCN}\cdots\text{HX}$  complexes are assumed to be hydrogen-bonded with little extent of  $\text{H}^+$  transfer from HX to N, the nuclear quadrupole coupling constants  $\chi_{aa}(\text{X})$  set out in Table 1 show that the three ammonium halides  $\text{H}_3\text{N}\cdots\text{HX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) have values that are little different from those of the corresponding complexes  $\text{HCN}\cdots\text{HX}$ . This result indicates only minor differences of ionic character  $\text{H}_3\text{NH}^+\cdots\text{X}^-$  in each ammonium halide from that of its  $\text{HCN}\cdots\text{HX}$  analogue.

On the other hand, complete methylation of  $\text{H}_3\text{N}\cdots\text{HX}$  to give the trimethylammonium halide  $(\text{CH}_3)_3\text{N}\cdots\text{HX}$  leads to a large decrease in magnitude of  $\chi_{aa}(\text{X})$  (see Table 1) from that of the corresponding ‘normal’ hydrogen-bonded complex  $\text{HCN}\cdots\text{HX}$ . Also included in Table 1 are the  $\chi_{aa}(\text{X})$  for the NaX ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), all of which can be described in reasonable approximation as the ion pair  $\text{Na}^+\cdots\text{X}^-$  in the vapour phase. Table 1 shows in particular that the  $\chi_{aa}(\text{X})$  value for  $(\text{CH}_3)_3\text{N}\cdots\text{HI}$  is very close in sign and magnitude to that of NaI, thereby indicating that in trimethylammonium iodide, the proton has been largely transferred from HI to trimethylamine and that it is best described as almost an ion pair in the vapour phase. Detailed arguments set out in Ref. [29] conclude that the contribution of the ionic structure  $(\text{CH}_3)_3\text{NH}^+\cdots\text{X}^-$  to the trimethylammonium halide  $(\text{CH}_3)_3\text{N}\cdots\text{HX}$  increases from approximately 0% for  $\text{X} = \text{F}$ , to  $\sim 60\%$  for  $\text{X} = \text{Cl}$ ,  $\sim 80\%$  for  $\text{X} = \text{Br}$  to  $\sim 90\%$  for  $\text{X} = \text{I}$ . These values and the conclusion that the  $\text{H}_3\text{N}\cdots\text{HX}$  exhibit little proton transfer are also discussed in Ref. [29] in the light of the energies required for the processes,



which are calculated from the known values of the proton affinity of trimethylamine, the dissociation energies of HX, the ionisation potential of H and the electron affinities of X.

After publication of the review<sup>29</sup> on the nature of the ammonium and methylammonium halides in 1993, there was a gradual change in the direction of the microwave spectroscopy research at the University of Exeter. When using the fast-mixing nozzle to examine the trimethylammonium halides, it became clear that, if precipitation of the solid phase of these systems could be thereby avoided, then perhaps using the same device it might be possible to observe the rotational

**Table 1:** Nuclear quadrupole coupling constants of ammonium halides and trimethylammonium halides compared with those of various model systems.

Molecule	X = Cl	X = Br	X = I
	$\chi_{aa}({}^{35}\text{Cl})/\text{MHz}$	$\chi_{aa}({}^{79}\text{Br})/\text{MHz}$	$\chi_{aa}({}^{127}\text{I})/\text{MHz}$
HX	$-67.619$	$444.681$	$-1823.4$
$\text{HC}^{14}\text{N}\cdots\text{HX}$	$-53.720$	$356.232$	$-1475.7$
$\text{H}_3^{14}\text{N}\cdots\text{HX}$	$-47.607$	$301.777$	$-1324.89$
$(\text{CH}_3)_3^{14}\text{N}\cdots\text{HX}$	$-21.625$	$99.645$	$-341.204$
$\text{Na}^+\cdots\text{X}^-$	$-5.643$	$48.508$	$-262.14$



spectra of complexes formed between molecules that react rapidly together when mixed normally. An obvious choice for reactive pairs was di-halogen molecules and Lewis bases such as ammonia, phosphine, ethene and ethyne. In fact, the fast-mixing nozzle worked very well for arresting the reaction between the components, so that the spectra of the complexes formed prior to reaction could be observed. Such 'pre-reactive' complexes were of possible interest to those investigating chemical kinetics. The first system we studied was  $\text{H}_3\text{P}\cdots\text{Cl}_2$ .<sup>30</sup> In the period between 1993 and 2005, we investigated a large number of complexes of the type  $\text{B}\cdots\text{Cl}_2$ ,  $\text{B}\cdots\text{BrCl}$ ,  $\text{B}\cdots\text{Br}_2$ , and  $\text{B}\cdots\text{ICl}$  by systematically varying the Lewis base B over a wide range, including  $\text{N}_2$ , CO, ethyne, ethene, cyclopropane,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ .

The fast-mixing nozzle even proved effective as a means of observing complexes formed by  $\text{F}_2$  or ClF with the simple Lewis bases. Mixing such bases with  $\text{F}_2$  or ClF in the gas phase under normal circumstances leads to violent chemical reaction in many cases. With ClF as the Lewis acid, we detected and analysed the rotational spectra of complexes with many different Lewis bases, not only those listed above but also methane, allene, butadiene, methylenecyclopropane, formaldehyde, oxirane, 2,5-dihydrofuran, trimethylamine, thiirane, sulphur dioxide, furan, thiophene and benzene. The additional Lewis bases were chosen either for their simplicity or to illustrate a specific aspect of the interaction. For example, butadiene has a pair of conjugated  $\pi$ -bonds, allene has a pair of cumulative  $\pi$ -bonds, while methylenecyclopropane can be viewed as possessing cumulative  $\pi$ - and pseudo- $\pi$  bonds. Oxirane and 2,5-dihydrofuran are postulated to have different angles between the non-bonding electron pairs on O, as referred to earlier; methane, ethyne, ethene, and benzene are prototype hydrocarbons, furan is a simple heteroaromatic molecule, and so on. The corresponding set of hydrogen-bonded complexes  $\text{B}\cdots\text{HCl}$  were characterised previously.

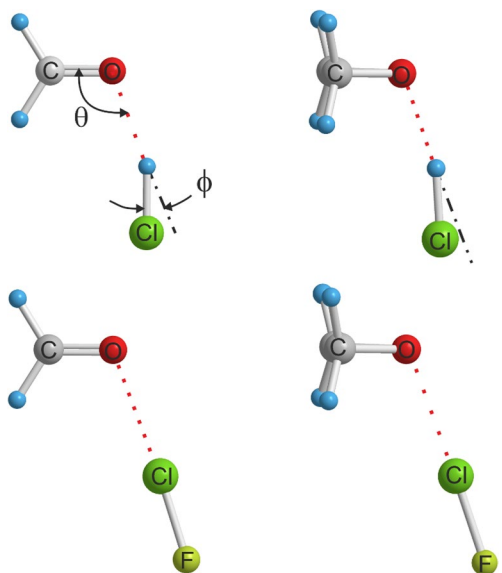
It became clear during the period 1993–2004 that complexes  $\text{B}\cdots\text{HCl}$  and  $\text{B}\cdots\text{ClF}$  were isomorphous for a given B and that there existed in the latter group of complexes a halogen bond similar to the hydrogen bond, as was made clear in a paper in 1998<sup>31</sup> concerned with  $\pi$ -electron donors complexed with ClF, then again, more generally, in a comprehensive review<sup>32</sup> in 1999 and updated and consolidated in 2007.<sup>33</sup> This isomorphism is also evident among the other  $\text{B}\cdots\text{HX}$  and  $\text{B}\cdots\text{XY}$  series but these series were less extensively investigated. All three articles pointed to the parallelism of several properties (including

geometry) of the two series and made the detailed case for a halogen bond  $\text{B}\cdots\text{XY}$  that is the analogue of the hydrogen-bond  $\text{B}\cdots\text{HX}$ . Even partial halogen-ion transfer to N was detected in the complexes  $(\text{CH}_3)_3\text{N}\cdots\text{F}-\text{F}$  and  $(\text{CH}_3)_3\text{N}\cdots\text{Cl}-\text{F}$ , parallel to the partial proton transfer deduced earlier for the  $(\text{CH}_3)_3\text{N}\cdots\text{HX}$ .

One important difference noted between the pairs in the  $\text{B}\cdots\text{ClF}$  and  $\text{B}\cdots\text{HCl}$  series<sup>32, 33</sup> is the propensity (when symmetry allows) for the  $\text{Z}\cdots\text{H}-\text{Cl}$  nuclei (where Z is the acceptor atom or centre of the Lewis base) to deviate from collinearity in the  $\text{B}\cdots\text{HCl}$  complex, while the corresponding system  $\text{B}\cdots\text{ClF}$  remains collinear. The angular deviation  $\phi$  from collinearity can be accurately determined from the off-diagonal component of the Cl-nuclear quadrupole coupling constant in molecules of  $\text{C}_s$  symmetry, as demonstrated for  $\text{B}\cdots\text{HX}$  in a Faraday Discussion paper.<sup>34</sup> The results for oxirane $\cdots\text{HCl/ClF}$  and formaldehyde $\cdots\text{HCl}$  are illustrated in scale diagrams in Fig. 7.  $\theta$  is the angle (according to the rules discussed earlier) made by the non-bonding electron pairs on O with the  $\text{C}_2$  axis of the Lewis base. It is essentially identical for the ClF and HCl complexes when B = formaldehyde. The same is true for B = oxirane. For both Lewis bases, however, the angular deviation  $\phi$  of the  $\text{Z}\cdots\text{H}-\text{Cl}$  nuclei from collinearity is close to  $20^\circ$ ; while for the ClF complexes, the deviations are only  $\sim 3^\circ$ . Clearly, secondary interactions of  $\text{Cl}^{\delta-}$  of HCl with the electrophilic H atoms of the Lewis base are significant in the HCl complexes, but not so for  $\text{F}^{\delta-}$  of ClF in the halogen-bonded complexes. This difference in behaviour of  $\text{B}\cdots\text{ClF}$  and  $\text{B}\cdots\text{HCl}$  for a given B was later explained by Anthony Stone in terms of a resistance to bending of the  $\text{Z}\cdots\text{Cl}-\text{F}$  system that result from a repulsive interaction of Cl with the Lewis base.<sup>35</sup> Such an interaction is effectively absent in the  $\text{B}\cdots\text{HCl}$  complexes, presumably because  $\text{H}^{\delta+}$  is essentially denuded of electrons.

In 2002/2003 the pulsed-nozzle, F–T cavity spectrometer in Exeter was upgraded to incorporate improvements in both the sensitivity and resolution, as included in the spectrometer developed by Jens-Uwe Grabow in the Kiel group (to whom thanks for his generous advice to us when we were making the upgrade).

The superb resolution of the upgraded instrument is well illustrated by the recording displayed in Fig. 8, which shows the five components (each component is doubled by a Doppler effect) of the  $J=1 \leftarrow 0$  transition of  $^{16}\text{O}^{12}\text{C}\cdots\text{D}^{19}\text{F}$ . The observed hyperfine structure arises from D-nuclear quadrupole coupling and D,F

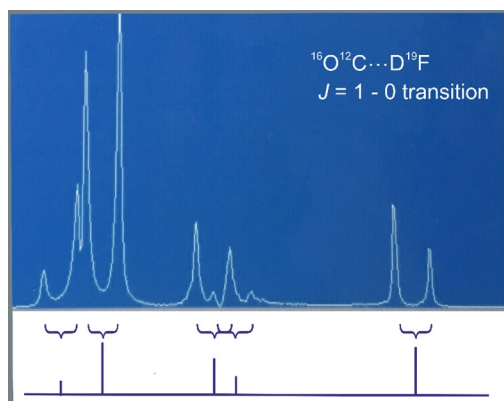


**Figure 7:** Nonlinear hydrogen bonds formed by HCl with formaldehyde and oxirane compared with the almost linear halogen bonds formed by ClF with these Lewis bases. The angles  $\theta$  are almost invariant for the pair of formaldehyde complexes [ $70.0(1)^\circ$  and  $69.1(7)^\circ$  for HCl and ClF, respectively], while the nonlinearities  $\phi$  are  $20.5(8)^\circ$  and  $3.2(7)^\circ$  for HCl and ClF complexes. The corresponding pairs when oxirane is the Lewis base are  $\theta=69.1(1)^\circ$  and  $67.3(1)^\circ$  for HCl and ClF, respectively, but  $\phi=16.5(1)^\circ$  and  $2.9(1)^\circ$  for HCl and ClF, respectively

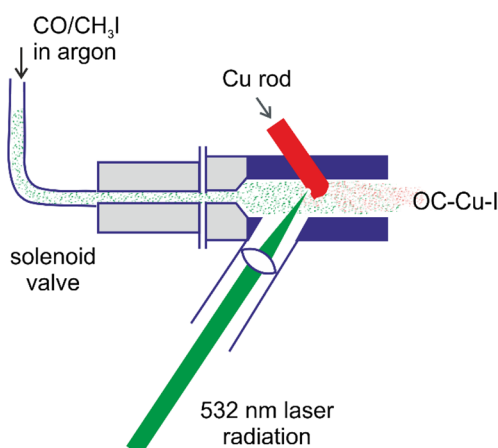
spin–spin coupling. The components are spread over a frequency range of only  $\sim 300$  kHz and the full-width at half height of each component is only  $\sim 5$  kHz. Robin Batten, the Department's IT expert, was responsible for writing and installing all the new softwares concerned with the digitisation of signals, their Fourier transformation and their display.

### 3 University of Bristol 2005–Present

Just before the University of Exeter closed its Chemistry Department in 2005 and I transferred to the University of Bristol, we fitted a solenoid valve/laser ablation system into the upgraded spectrometer. This device, shown in a schematic diagram in Fig. 9, plugs into a centrally placed hole in the back of one of the Fabry–Perot mirrors. A pulse of a gas mixture consisting of, for example, 2% carbon monoxide and 0.5% methyl iodide in argon from the solenoid valve passes over the surface of, say, a copper rod which is ablated by a suitably timed pulse of 532 nm radiation from a Nd-YAG laser. Ablated Cu atoms abstract iodine from methyl iodide to give cuprous iodide, which then reacts with carbon monoxide to produce  $\text{OC}\cdots\text{Cu-I}$ , the rotational spectrum of which can then be observed in the usual way.<sup>36</sup>



**Figure 8:** The 5 hyperfine components of the  $J=1 \leftarrow 0$  transition of  $^{16}\text{O}^{12}\text{C}\cdots\text{D}^{19}\text{F}$  arising from D nuclear quadrupole coupling and D, F nuclear spin–spin coupling observed with the upgraded pulsed-nozzle, F–T microwave spectrometer at the University of Exeter. Each component is a doublet as a result of a Doppler effect. The frequency range in the diagram is  $\sim 300$  kHz and the full-width at half height of each separate line is only  $\sim 5$  kHz



**Figure 9:** A schematic diagram of the laser ablation nozzle used in the pulsed-nozzle, F–T microwave spectrometer at the University of Exeter to allow the observation of the rotational spectra of 'coinage-metal' complexes such as  $\text{OC}\cdots\text{CuI}$ . See text and Ref. [36] for discussion

The rotational spectra of complexes formed by a rare-gas atom or CO with coinage-metal halides MX ( $M = \text{Cu, Ag or Au}$ ;  $X = \text{F, Cl, or Br}$ ) were investigated by the late Michael Gerry's group at the University of British Columbia, with the first complexes (rare gases...MX) observed in 1999 and first reported in 2000.<sup>37</sup> The interaction of B and MX in B...MX is formally of the non-covalent type, albeit much stronger than that in most hydrogen or halogen-bonded complexes. Once in Bristol, I began a collaboration with Nick Walker with the aim of extending the range of complexes B...MX to include Lewis bases other than rare gases and carbon monoxide and thereby allowing a systematic investigation of this 'coinage-metal bond'. The results were then to be compared with those of hydrogen- and halogen-bonded analogues to find any similarities or differences. So far, the rotational spectra of complexes involving Lewis bases  $B = \text{N}_2$ , ethene, ethyne, cyclopropane,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$  and  $\text{NH}_3$  with several MX ( $\text{MCl, MF, MI}$  for  $M = \text{Cu or Ag}$ ) have been detected and analysed to give various properties of the B...MX, a task facilitated later by use of a chirped-pulse, broadband F–T microwave spectrometer, built by Nick Walker in Bristol<sup>38</sup> but now residing at Newcastle University, together with the much-travelled, but now semi-retired, Balle–Flygare instrument. Generalisations about the properties of a wide range of B...MX have been made and described in a recent Perspectives article,<sup>39</sup> which points to the isomorphism among hydrogen-bonded complexes B...HX, halogen-bonded complexes B...XY and coinage-metal complexes B...MX. Ref. [39] also proposes a generalised nomenclature for the various types of non-covalent interaction, including tetrel, pnictogen and chalcogen bonds. The last three types were named only recently, but a significant number of them were identified and characterised in the gas phase by means of their rotational spectra some years ago.<sup>40</sup>

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Bristol. They were not large in number but were uniformly excellent as colleagues. The following (approximate) timeline mentions the areas to which they contributed and the location in which they conducted their research.

**Hydrogen bond: UCL 1972–1984** John Bevan, Stephen Rogers, Andreas Georgiou, Krini Georgiou, Zybsyk Kisiel, Johan Mjöberg, Charles Willoughby, Philip Cope, Hazel North, Ronald Collins.

**Hydrogen bond: Exeter 1984–1989** Elizabeth Goodwin, Annette Fillery-Travis, Nigel Howard, Bill Rothwell, Andrew Suckley, Andrew Wallwork.

**Halogen and hydrogen bonds: Exeter 1990–2005** Joanna Thorn, David Lister, Chris Rego, Hugh Warner, Hannelore Bloemink, Kelvin Hinds, Gina Cotti, Christopher Evans, Sean Peebles, Stephen Cooke, Gary Corlett, Eric Waclawik, Paolo Ottaviani, George Cole, James Davey, Jenny Thumwood, Susan Batten.

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1990–2005) and Bristol (2005–2008). In 1980, he spent a sabbatical year working in the laboratory of Willis Flygare at the University of Illinois (Champaign–Urbana). He has been Tilden and Liversidge Lecturers of the Royal Society of Chemistry (1990 and 2012, respectively), EPSRC Senior Fellow (1997–2002), was elected a Fellow of the Royal Society in 2000 and is currently Senior Research Fellow at Bristol. His research interests are centred on systematic investigations (mainly by rotational spectroscopy) of non-covalent interactions.